

## 1.0 Introduction

The objective of the report is to provide a reasoned and documented discussion on the technical issues associated with the measurement and selection of partition (or distribution) coefficient,  $K_d$ ,<sup>1,2</sup> values and their use in formulating the retardation factor,  $R_f$ . The contaminant retardation factor ( $R_f$ ) is the parameter commonly used in transport models to describe the chemical interaction between the contaminant and geological materials (*i.e.*, soil, sediments, rocks, and geological formations, henceforth simply referred to as soils<sup>3</sup>). It includes processes such as surface adsorption, absorption into the soil structure, precipitation, and physical filtration of colloids. Specifically, it describes the rate of contaminant transport relative to that of groundwater. This report is provided for technical staff from EPA and other organizations who are responsible for prioritizing site remediation and waste management decisions. The two-volume report describes the conceptualization, measurement, and use of the  $K_d$  parameter; and geochemical aqueous solution and sorbent properties that are most important in controlling the adsorption/retardation behavior of a selected set of contaminants.

This review is not meant to assess or judge the adequacy of the  $K_d$  approach used in modeling tools for estimating adsorption and transport of contaminants and radionuclides. Other approaches, such as surface complexation models, certainly provide more robust mechanistic approaches for predicting contaminant adsorption. However, as one reviewer of this volume noted, “ $K_d$ ’s are the coin of the realm in this business.” For better or worse, the  $K_d$  model is integral part of current methodologies for modeling contaminant and radionuclide transport and risk analysis.

The  $K_d$  concept, its use in fate and transport computer codes, and the methods for the measurement of  $K_d$  values are discussed in detail in Volume I and briefly introduced in Chapters 2 and 3 in Volume II. Particular attention is directed at providing an understanding of: (1) the use of  $K_d$  values in formulating  $R_f$ , (2) the difference between the original thermodynamic  $K_d$  parameter derived from the ion-exchange literature and its “empiricized” use in contaminant transport codes, and (3) the explicit and implicit assumptions underlying the use of the  $K_d$  parameter in contaminant transport codes.

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<sup>1</sup> Throughout this report, the term “partition coefficient” will be used to refer to the  $K_d$  “linear isotherm” sorption model. It should be noted, however, that the terms “partition coefficient” and “distribution coefficient” are used interchangeably in the literature for the  $K_d$  model.

<sup>2</sup> A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B

<sup>3</sup> The terms “sediment” and “soil” have particular meanings depending on one’s technical discipline. For example, the term “sediment” is often reserved for transported and deposited particles derived from soil, rocks, or biological material. “Soil” is sometimes limited to referring to the top layer of the earth’s surface, suitable for plant life. In this report, the term “soil” was selected with concurrence of the EPA Project Officer as a general term to refer to all unconsolidated geologic materials.

The  $K_d$  parameter is very important in estimating the potential for the adsorption of dissolved contaminants in contact with soil. As typically used in fate and contaminant transport calculations, the  $K_d$  is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. Soil chemists and geochemists knowledgeable of sorption processes in natural environments have long known that generic or default  $K_d$  values can result in significant errors when used to predict the impacts of contaminant migration or site-remediation options. To address some of this concern, modelers often incorporate a degree of conservatism into their calculations by selecting limiting or bounding conservative  $K_d$  values. For example, the most conservative (*i.e.*, maximum) estimate from the perspective of off-site risks due to contaminant migration through the subsurface natural soil and groundwater systems is to assume that the soil has little or no ability to slow (retard) contaminant movement (*i.e.*, a minimum bounding  $K_d$  value). Consequently, the contaminant would travel in the direction and at the rate of water. Such an assumption may in fact be appropriate for certain contaminants such as tritium, but may be too conservative for other contaminants, such as thorium or plutonium, which react strongly with soils and may migrate  $10^2$  to  $10^6$  times more slowly than the water. On the other hand, when estimating the risks and costs associated with on-site remediation options, a maximum bounding  $K_d$  value provides an estimate of the maximum concentration of a contaminant or radionuclide sorbed to the soil. Due to groundwater flow paths, site characteristics, or environmental uncertainties, the final results of risk and transport calculations for some contaminants may be insensitive to the  $K_d$  value even when selected within the range of technically-defensible, limiting minimum and maximum  $K_d$  values. For those situations that are sensitive to the selected  $K_d$  value, site-specific  $K_d$  values are essential.

The  $K_d$  is usually a measured parameter that is obtained from laboratory experiments. The 5 general methods used to measure  $K_d$  values are reviewed. These methods include the batch laboratory method, the column laboratory method, field-batch method, field modeling method, and  $K_{oc}$  method. The summary identifies what the ancillary information is needed regarding the adsorbent (soil), solution (contaminated ground-water or process waste water), contaminant (concentration, valence state, speciation distribution), and laboratory details (spike addition methodology, phase separation techniques, contact times). The advantages, disadvantages, and, perhaps more importantly, the underlying assumptions of each method are also presented.

A conceptual overview of geochemical modeling calculations and computer codes as they pertain to evaluating  $K_d$  values and modeling of adsorption processes is discussed in detail in Volume I and briefly described in Chapter 4 of Volume II. The use of geochemical codes in evaluating aqueous speciation, solubility, and adsorption processes associated with contaminant fate studies is reviewed. This approach is compared to the traditional calculations that rely on the constant  $K_d$  construct. The use of geochemical modeling to address quality assurance and technical defensibility issues concerning available  $K_d$  data and the measurement of  $K_d$  values is also discussed. The geochemical modeling review includes a brief description of the EPA's MINTEQA2 geochemical code and a summary of the types of conceptual models it contains to quantify adsorption reactions. The status of radionuclide thermodynamic and contaminant adsorption model databases for the MINTEQA2 code is also

reviewed.

The main focus of Volume II is to: (1) provide a “thumb-nail sketch” of the key geochemical processes affecting the sorption of a selected set of contaminants; (2) provide references to related key experimental and review articles for further reading; (3) identify the important aqueous- and solid-phase parameters controlling the sorption of these contaminants in the subsurface environment; and (4) identify, when possible, minimum and maximum conservative  $K_d$  values for each contaminant as a function key geochemical processes affecting their sorption. The contaminants chosen for the first phase of this project include cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium ( $^3\text{H}$ ), and uranium. The selection of these contaminants by EPA and PNNL project staff was based on 2 criteria. First, the contaminant had to be of high priority to the site remediation or risk assessment activities of EPA, DOE, and/or NRC. Second, because the available funding precluded a review of all contaminants that met the first criteria, a subset was selected to represent categories of contaminants based on their chemical behavior. The six nonexclusive categories are:

- ☐ Cations - cadmium, cesium, plutonium, strontium, thorium, and uranium(VI).
- ☐ Anions - chromium(VI) (as chromate) and uranium(VI).
- ☐ Radionuclides - cesium, plutonium, radon, strontium, thorium, tritium ( $^3\text{H}$ ), and uranium.
- ☐ Conservatively transported contaminants - tritium ( $^3\text{H}$ ) and radon.
- ☐ Nonconservatively transported contaminants - other than tritium ( $^3\text{H}$ ) and radon.
- ☐ Redox sensitive elements - chromium, plutonium, and uranium.

The general geochemical behaviors discussed in this report can be used by analogy to estimate the geochemical interactions of similar elements for which data are not available. For example, contaminants present primarily in anionic form, such as Cr(VI), tend to adsorb to a limited extent to soils. Thus, one might generalize that other anions, such as nitrate, chloride, and U(VI)-anionic complexes, would also adsorb to a limited extent. Literature on the adsorption of these 3 solutes show no or very little adsorption.

The concentration of contaminants in groundwater is controlled primarily by the amount of contaminant present at the source; rate of release from the source; hydrologic factors such as dispersion, advection, and dilution; and a number of geochemical processes including aqueous geochemical processes, adsorption/desorption, precipitation, and diffusion. To accurately predict contaminant transport through the subsurface, it is essential that the important geochemical processes affecting contaminant transport be identified and, perhaps more importantly, accurately described in a mathematically and scientifically defensible manner. Dissolution/precipitation and adsorption/desorption are usually the most important processes affecting contaminant interaction with soils. Dissolution/precipitation is more likely to be the key process where chemical nonequilibrium exists, such as at a point source, an area where high contaminant concentrations exist, or where steep pH or oxidation-reduction (redox) gradients exist. Adsorption/desorption will likely be the key process controlling contaminant migration in areas where chemical steady state exists, such as in areas far from the point source. Diffusion flux spreads solute via

a concentration gradient (*i.e.*, Fick's law). Diffusion is a dominant transport mechanism when advection is insignificant, and is usually a negligible transport mechanism when water is being advected in response to various forces.